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**MONSANTO/WASHINGTON UNIVERSITY**

**ONR/ARPA ASSOCIATION**

# THE EFFECTS OF SOLVENTS AND STRESS ON THE STRESS-RUPTURE LIFE OF GLASS-EPOXY COMPOSITES

BY

D. C. RUHMANN
E. M. WU

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PROGRAM MANAGER

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JANUARY 1971

MONSANTO/WASHINGTON UNIVERSITY ASSOCIATION
HIGH PERFORMANCE COMPOSITES PROGRAM
SPONSORED BY ONR AND ARPA
CONTRACT NO. N00014-67-C-0218, ARPA ORDER 876
ROLF BUCHDAHL, PROGRAM MANAGER

MONSANTO RESEARCH CORPORATION
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# FOREWORD

The research reported herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

The prime contractor is Monsanto Research Corporation. The Program Manager is Dr. Rolf Buchdahl (phone 314-694-4721).

The contract is funded for $7,000,000 and expires 30 April 1972.

# THE EFFECTS OF SOLVENTS AND STRESS ON THE STRESS-RUPTURE LIFE OF GLASS-EPOXY COMPOSITES

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## ABSTRACT

This paper is concerned with the combined effect of an active environment and stress on the survival life of a polymeric composite material. The object of this investigation is to extend the well known kinetic theory of rate-dependent rupture to anisotropic composites in active chemical environments, and to establish the operational technique for one system of environment and composite material. Observations on the statistical variability of the rupture processes are given. The reduction in the life of a homogeneous epoxy matrix (60% Epon 815-40% Versamid 140) and that of a unidirectional glass fiber-reinforced epoxy in benzene was experimentally observed for several stress levels. It is hoped that these results can eventually be linked together through micro-mechanics analysis. Significant decreases in survival life of the matrix at several stress levels in the benzene environment were observed. These reductions in life cannot be predicted nor explained from sorption data characterized as Alfrey's Case II transport. Stress rupture experiments were performed for unidirectional composites at $0^{\circ}$, $45^{\circ}$ and $90^{\circ}$. Experimental results showed the decrease in life is strongly dependent on the angular orientation of the composite both for the inert and active environment. This suggested a tensorial

characteristic must be incorporated into the classical shift factor. Further work required to characterize this anisotropic effect is suggested.

(Contribution HPC 70-134 from the Monsanto/Washington University Association sponsored by the Advanced Research Projects Agency, Department of Defense, under Office of Naval Research Contract No N00014-67-C-0218.)

# THE EFFECTS OF SOLVENTS AND STRESS ON THE STRESS-RUPTURE LIFE OF GLASS-EPOXY COMPOSITES

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## INTRODUCTION

The phenomenon of creep fracture, i.e. the delayed fracture of materials under constant stress, is a very important consideration in the engineering application of many time-dependent materials including polymers and polymeric composites. In addition, many applications call for such a material to be used in a chemically active environment which shortens the life expectancy.

This paper is concerned with the combined effect of an active environment and stress on the survival life of a polymeric composite. The objective of this investigation is to explore the operational techniques which are necessary to extend the kinetic theory of rate-dependent rupture [1,2,3] to include anisotropic and environmental effects. The time to rupture, $t_R$, is defined as:

$$t_R = A\, f(\sigma, T, \theta, C)\, e^{\frac{\Delta H}{RT}} \qquad (1)$$

where:

A = Material parameter
$\sigma$ = Stress
T = Temperature
$\theta$ = Fiber orientation
C = Chemical effect
$\Delta H$ = Activation energy
R = Gas constant

A shortcoming of equation (1), however, is that it does not include the observation of the statistical variability of the rupture process. Therefore, the time dependent rupture model proposed by Halpin, et al [4], which includes the stochastic process effect will be used in conjunction with equation (1) to analyze the stress-rupture results. It is hoped the techniques obtained for the system in this investigation can be generalized to other systems.

The samples used in this study were homogeneous epoxy and unidirectional glass fiber-reinforced epoxy resin (60% Epon® 815 - 40% Versamid® by weight). The active environment was that of liquid benzene at room temperature.

Tensile creep rupture tests at different stress levels are performed for both the pure resin and composite specimens in an inert environment. These results are compared to similar experiments performed in the active environment. In order to qualitatively account for the effect of the environment, the kinetics of sorption of benzene by the pure resin and the composite specimens are studied. Combining the studies, the hypothesis that environment reduces the survival life through the generation of swelling stresses can be examined.

## EXPERIMENTAL

Sample Preparation:

The epoxy resin used in this study consisted of a mixture of 60% by weight Shell Epon® 815 and 40% General Mills' Versamid® 140. Chemical reaction between the amino groups of the Versamid® resin and epoxide groups of the Epon® 815 resin results in a cross-linked polymer. Mixing was conducted under vacuum to minimize the presence of voids, and the mixture was cast between parallel plated spaced 1/8 inch apart and cured such that complete cross-linking was achieved [5].

The composite system studied had the above epoxy as the matrix with the reinforcement being continuous unidirectional glass fibers. Composite samples were made by filament winding five layers of PPG 1064 T 4 glass. A PPG proprietary glass surface treatment was used to promote adhesion at the fiber-matrix interface. The resulting unidirectionally reinforced epoxy sheet was approximately .05 inches thick. Fiber concentration, determined by burn-off, was found to be 56 ± 1% by volume. The cure cycle was identical to that of the homogeneous material.

Tensile stress-rupture specimens were cut from the homogeneous and composite sheets and machined to the familiar reduced cross section (dog-bone) geometry in accordance with A.S.T.M. Standard D 638, i.e. a gauge length of 2 1/4 inches with radii of 3 inches.

Experimental Procedures:

A. Static Tensile Tests:

The ultimate tensile strength of the composite material was determined for fiber orientations of 0, 45, and 90 degrees. The tensile tests were conducted on an Instron Universal Testing Machine. The time to fracture was maintained at approximately five minutes for specimens of all orientations by varying the cross-head speed.

B. Stress-Rupture Tests:

The stress-rupture tests were also conducted on an Instron testing machine. A constant tensile load with error less than 2% was applied to the test specimen. The raise time to reach maximum creep load was approximately 30 seconds. The active environment tests were performed by adapting a special grip and container assembly (shown schematically in Figure 1) to the testing machine. This assembly allowed the environment of benzene to be in contact with the stressed specimen until fracture. In order to prevent fracture in the gripping area, the grip areas were protected from benzene attack by the use of glycerin as shown in the figure.

C. Sorption Tests:

The kinetics of benzene sorption by the homogeneous matrix material was obtained by submersing rectangular specimens with approximate dimensions of 1/2" x 1" x 1/8" and round specimens with diameter of .55" in benzene at room temperature (24°C). The depth of penetration and swell as defined in Figure 2 were

measured at increasing time intervals. The measurements were made with a traveling stage optical micrometer with accuracy to ± .0001 inches. The gel-core interface was distinct making the measurement reproducible to the same accuracy.

The composite specimen sorption-kinetics data were obtained by placing rectangular specimens with dimensions about 1 3/4" x 3/8" x 1/8" in benzene. The specimens had fiber orientations varying from 0 to 90 degrees at 15 degree intervals (Figure 2b). The dilatation measurements (swell) were made with the same optical micrometer. The depth of penetration along the specimen length was not uniform, and the gel-core interface was not well defined. These facts caused the measurement of depth of penetration to be difficult and less reproducible than for the homogeneous specimens. The values of penetration reported are the averages of several measurements made with accuracy of ± .01 inches.

## RESULTS

In the study of creep and stress-rupture of materials, the use of a mechanical equation of state is well established [6,7]. The phenomenon of time-dependent fracture is describable in terms of the Arrhenius expression [8]:

$$K = Ae^{\frac{-Ea}{RT}} \qquad (2)$$

where:

K = Rate constant
A = Frequency factor
Ea = Activation energy
T = Absolute Temperature
R = Gas constant

The equation for time to rupture, equation (1), follows directly from equation (2). When the effects of chemical environments, c, and fiber orientation, $\theta$, are absent and at constant temperature, the function $f(\sigma, T, \theta, c)$ reduces to $f(\sigma)$. One form of $f(\sigma)$ commonly given in the literature [9,10] is:

$$f(\sigma) = \sigma^{-m} \qquad (3)$$

which implies that (at constant temperature):

$$t_R = A\sigma^{-m} \qquad (4)$$

Cameron [11] has shown that equation (4) fits the creep-rupture data he obtained on a system similar to that being studied in this work. It has also been shown that the effects of temperature on the stress-rupture results of homogeneous

polymeric materials can be superimposed through the use of the "time-temperature superposition principal" [12]. The shifting factors necessary for the above can be computed from the WLF equation [13]. Halpin [4] has shown the effect of stress may also be described in terms of a shift parameter.

In order to employ shift parameters to predict a physical process (such as fracture, in this case), it is necessary to establish that the physical process in question is the same within the time scale of the shift operation. Formulations of the form indicated by equations (1) or (4) only operate on the mean time to rupture and cannot distinguish the physical processes which cause rupture. It was shown by Wu and Halpin [14] that even at identical stress levels, rupture was a result of competing mechanisms of flaw growth and plastic flow. The different rupture processes manifest themselves in different cumulative distributions of survival lifetimes, $\frac{n(t)}{N_T}$. Figure 3 illustrates schematically the difference in these distributions for brittle fracture and plastic flow that were obtained from stress rupture tests of PMMA by Wu and Halpin [14]. Populations of specimens with identical distributions of creep rupture life showed similar fracture morphology and may indicate that the processes causing fracture are similar. It is therefore necessary to examine the distributions of lifetime curves before one can perform superposition via shift parameters to account for the effects of active environments.

A theoretical model proposed by Halpin *et al.* [4] is now used to describe the experimental results since this theory includes the observation of the statistical theory of fracture. Halpin has utilized the theory of stochastic processes to derive an expression for the cumulative distribution

$$\frac{n(t)}{N_T} = \exp(-kt^N) \tag{5}$$

where

$$K = \text{Const} \cdot G / a_T \cdot a_E \cdot a_c$$

and

$n(t)$ = Number of specimens surviving at time t

$N_T$ = Total number of specimens

$G$ = Defect growth vector

$a_T$ = Time-temperature reduction parameter

$a_E$ = Shift factor for magnitude of excitation

$a_c$ = Chemical shift factor

$N$ = Adjustable parameter characterizing fracture process*

It can be shown that for a change in stress levels $a_E = a_\sigma$ and that the mean time to failure, as described by Halpin's theory, assumes the form of equation (4).

A series of stress-rupture tests were performed on the homogeneous epoxy specimens at two stress levels, with and

* For example N = 1, 2, and 3 may be interpreted [4] as one, two or three dimensional flaw growth respectively. Non-integer values of N may be interpreted [14] as a result of competing flaw growth and plastic flow.

without the presence of benzene. The objectives of these tests were twofold; first to determine the effect of benzene on mean log-time to failure and second to establish the cumulative distribution function for the fracture process under the various conditions of testing. The two stress levels used in the study were 4500 and 5000 PSI. The results of the stress-rupture tests are shown in Figure 4 where the normalized survival population, i.e. the number of specimens surviving at time t, divided by the total population, N, is plotted versus the log-time to failure. The cumulative distribution (or normalized survival population), $\frac{n(t)}{N_T}$, is seen to have the sigmoidal shape predicted by equation (5). The decrease in survival life as a result of the active environment of benzene is apparent for both stress levels.

To determine if the distributions are similar, one can take the log-log of both sides of equation (5). Performing this operation:

$$\log \left[\log \left(\frac{n(t)}{N_T}\right)\right] = \log (.43K) + N \log (t) \qquad (6)$$

Thus, the slope obtained from a plot of $\log \left[\log \left(\frac{n(t)}{N_T}\right)\right]$ versus log t is equal to N, the power of t in equation (5). If the processes causing fracture are similar, the distribution, and hence the value of N, should also be similar. To analyze the distributions obtained with the various test conditions, the log-log of the cumulative distribution $\left(\frac{n(t)}{N_T}\right)$ has been plotted versus log t in Figure 5. The first observation is

that the two distributions for the specimens tested without benzene at 4500 and 5000 PSI respectively are similar, with each having a value of N equal to two. This value of N corresponds to two dimensional defect growth or plastic flow. The concept of a linear shift parameter for stress is seen to be applicable to this material, i.e. the distribution has been linearly shifted on the time axis as a result of the change in stress level.

In contrast to the distributions obtained with the inert environment, specimens tested at the two stress levels above, but in the presence of benzene, had different distributions. As seen in Figure 4 the specimens tested at 5000 PSI in benzene had a distribution resulting in a value of N equal to three. Because the value of N has been increased to three from two, one cannot assume that the processes causing fracture are similar.

At 4500 PSI the presence of benzene has decreased the value of N to 2/3 from the value of two obtained from the distributions of specimens tested in air. Again, the fracture processes are not similar. Figure 5 clearly shows the large difference in distributions for the specimens tested in benzene at 4500 and 5000 PSI.

The reason for the large difference is not firmly established at this time. It may be interpreted that at the lower stress level, the active environment not only reduces the mean life,

but also changes the fracture mechanism toward brittle fracture. However, at the higher stress level, the plastic flow characteristic of fracture appeared to be retained.

The next experimental results to be discussed are concerned with the composite material. Anisotropic specimens previously described were used in the study. Table 1 shows the results of static tensile tests conducted to establish the ultimate tensile strengths for the three fiber orientations. The variation of strength with fiber angle is shown in Figure 6.

Stress-rupture tests were conducted in air and benzene environments at 79% of the ultimate tensile strengths. The values of stress used are given in Table 1.

The normalized survival population versus log-time to rupture curves obtained from the tests are shown in Figure 7. The reduction in life which results with the presence of benzene is apparent in this figure for specimens with orientation of 0 and 45 degrees.

It was not possible to obtain a distribution for 90° orientation in benzene at a stress of 79% tensile strength. These specimens fractured immediately upon being stressed. The largest value of stress which would sustain life in benzene was found to be only 40% of the ultimate tensile strength.

To compare the distributions obtained with and without benzene at the various fiber orientations, the log-log of the cumulative distribution, $\frac{n(t)}{N_T}$, was plotted versus log time to

rupture. These plots are seen in Figure 8. The value of N obtained for orientations equal to 45 and 90 degrees in an air environment was two. This value of N is exactly the same as that obtained for the distributions of the homogeneous specimens tested in air. A value of N equal to three was obtained for the 45 degree specimens when tested in the benzene environment. As was the case with the homogeneous material tested at 5000 PSI, the benzene environment increased the value of N for the $45^{\circ}$ orientation by one. The value of N for the 0 degree specimens tested in air and benzene was found to be 1/2.

The dependence of mean survival life at a stress level of 79% tensile strength on fiber orientation is shown in Figure 9 for both the active and inert environments. This figure reveals the necessity to include fiber orientation into the characterization of time dependent rupture of composite specimens. The static strength of composite materials as a function of fiber orientation has been recently shown to obey tensorial transformation rules [15]. It would be reasonable to expect the effect of anisotropy on stress-rupture results might also transform as above.

In order to relate the reduction of life in benzene to the rate of penetration of benzene into the specimen, the sorption kinetics of benzene into the homogeneous resin and the fiber composite were studied. Knowing the rate of penetration the

swelling stresses can be computed and the hypothesis that the environment reduce the life through the generation of swelling stress may be examined. The results of the diffusion experiments described earlier are shown in Figure 10 where depth of penetration with time is given. In Figure 10, the steady state rate of penetration is linear. This behavior has been designated Case II diffusion by Alfrey, Gurnee, and Lloyd [16]. The presence of a very sharp interface between the gel and core was observed. The interface was much the same as described by Alfrey *et al.* [16] and Kwei and co-workers [17,18]. Additional work of Kwei *et al.* [19] has shown an applied stress transverse to the direction of the moving gel-core interface does not alter the kinetics of Case II sorption. Hence, it will be assumed the kinetics of benzene sorption during stress-rupture tests were the same as that in the absence of externally applied stress.

Similar experiments were used to determine the kinetics of sorption for the anisotropic composite specimens. The results obtained for the depth of penetration with time are shown in Figure 11. The rate of penetration is more than four times greater along the fibers ($0^{o}$) than normal to them ($90^{o}$). The rate of penetration of the homogeneous material is approximately the same as the penetration rate normal to the fiber direction.

The mean time to failure of the homogeneous resin at 5000 PSI in benzene was less than 1/2 hour which would (from figure

10) allow a depth of benzene penetration less than .002 inches. Therefore the possibility of significant swelling stresses must be considered minimal. Similarly the extremely short duration of the 45 and 90° stress-rupture tests in benzene and the depths of penetration at these times would also rule out the possibility of significantly large swelling stresses. Therefore, the decreased life must be attributed to factors other than swelling stresses such as a decrease in the surface energy necessary for the formation of new surfaces.

## CONCLUSION

The presence of benzene greatly reduces the survival life of both homogeneous and composite specimens. This reduction in life cannot be attributed solely to the generation of swelling stress. This phenomena may be strongly influenced by the hypothesis that the surface energy necessary for the formation of new surfaces decreases in an active environment leading to a drastic reduction of survival life.

Analysis, of the various distributions obtained from stress-rupture tests revealed the following:

(1.) Homogeneous, 45 degree, and 90 degree specimens all had similar distributions when tested in air. The value of N was found to be approximately two which suggests a two-dimensional defect growth or plastic flow.

(2.) The presence of benzene resulted in a decrease in the mean log-time and a change in the value of N. The changes in the distribution of survival life (i.e. different values of N) of the homogeneous and anisotropic material with benzene indicates the concept of a linear shift factor for a benzene environment must be modified to include this phenomenon. It can be concluded that the presence of benzene changes the physical processes which cause fracture.

(3.) The distributions of life for the 0 degree specimens in both air and benzene are considerably broader than those obtained for the 45 and 90 degree specimens.

The inability of the 90 degree specimens to sustain loads in the presence of benzene suggests possible fiber-matrix interface separation due to the benzene. The fiber orientation was found to greatly influence a composite specimen's ability to endure loads for extended periods of time. This orientation effect existed in both the inert and active environments.

The sorption of benzene by the homogeneous epoxy material was found to be described as Case II, the limiting case of "anomalous" diffusion where the penetration is linear with time. The presence of fibers increased the rate of penetration, possibly due to channeling along the fiber-matrix interface.

To quantitatively study the change in the fracture processes as a result of the presence of benzene at various stress levels, additional specimens must be tested. The various cumulative distributions will be more well defined with the increased number of observations. Additional testing of the composite specimens is required at a different percentage of their ultimate tensile strengths. This testing will allow the formulation of equations similar to equation (4) for each fiber direction. This knowledge would facilitate the study of environmental and orientational effects on laminated plates having layers with various fiber orientations.

## ACKNOWLEDGMENT

This work is part of the study of composites supported by the Monsanto/Washington University Association sponsored by the Advanced Research Project Agency, Department of Defense and the Office of Naval Research under contract No. N00014-67-C-0218, formerly N00014-66-C-0045.

## REFERENCES


1. J. C. Halpin, Journal of Applied Physics, 35, 3133 (1964).
2. J. C. Halpin, Rubber Reviews of Rubber Chemical Technology, Vol. 38 (1965), p. 1007.
3. T. K. Kwei, Journal of Applied Polymer Science, 10, 1647 (1966).
4. J. C. Halpin and H. W. Polley, Journal of Composite Materials, 1, 64 (1967).
5. R. L. Kaas, Private Communication, Washington University.
6. F. K. G. Odquist, Mathematical Theory of Creep and Creep Rupture, Oxford University Press, 1966, p. 15.
7. S. Goldfein, Journal of Applied Polymer Science, 10, 1737 (1966).
8. W. J. Moore, Physical Chemistry, Prentice-Hall, 1960, p. 546.
9. G. M. Bartenev and Yu S. Zuyev, Strength and Failure of Visco-Elastic Materials, Pergamon Press, Oxford, 1968, p. 273.
10. J. B. Conway, Numerical Methods for Creep and Rupture Analysis, Gordon and Breach, New York.
11. J. B. Cameron, Directory of Materials Report No. 145, Ministry of Technology, NASA File No. N68 24904, June 1967.
12. P. Mears, Polymers: Structure and Bulk Properties, D. Van Nostrand Company Ltd., London, 1967, p. 293.
13. M. L. Williams, R. F. Landel and J. D. Ferry, Journal of American Chemical Society, 77, 3701 (1955).
14. E. M. Wu and J. C. Halpin, to be published.
15. S. Tsai and E. M. Wu, Journal of Composite Materials, 5 (1971).
16. T. Alfrey, Jr., E. F. Gurnee and W. G. Lloyd, Journal of Polymer Science, C12, 249 (1966).
17. T. K. Kwei and H. M. Zupko, Journal of Polymer Science A-1, 7, 867 (1969).

18. H. L. Frisch, T. T. Wang and T. K. Kwei, Journal of Polymer Science A-1, 7, 879 (1969).

19. T. K. Kwei, T. T. Wang, H. N. Zupko, and H. L. Frisch, submitted to Journal of Polymer Science B for publication.

| Orientation (Degrees) | Number Observations | Mean Ultimate Tensile Strength (PSI) | Standard Deviation | 79% Tensile Strength |
|---|---|---|---|---|
| 0 | 8 | 134,000 | 4031 | 106,000 |
| 45 | 12 | 8,590 | 424 | 6,790 |
| 90 | 10 | 8,350 | 309 | 6,600 |

Table 1. Ultimate Tensile Strength of Anisotropic Composites

## LIST OF FIGURES


Figure 1. Schematic of environmental testing container and specimen grip assembly.

Figure 2. Schematic of specimens during sorption tests showing depth of penetration and swell. (a) Pure epoxy resin (b) Composite specimen.

Figure 3. Schematic representation of differences in the cumulative distributions for brittle and ductile rupture (Wu and Halpin [14]).

Figure 4. Normalized survival population versus log-time to failure in air and benzene for pure epoxy at stress levels of 4500 and 5000 PSI.

Figure 5. Log-log of the cumulative distribution, $\frac{n(t)}{N_T}$, versus log-time to failure for pure resin at stress levels of 4500 and 5000 PSI in both air and benzene.

Figure 6. Effect of fiber orientation on the ultimate tensile strength of composite specimens.

Figure 7. Normalized survival population versus log time to failure in both air and benzene for specimens tested at 79% ultimate tensile strength at each orientation.

Figure 8. The log log of the cumulative distribution versus log time to rupture for composite specimens tested at 79% ultimate tensile strength for each orientation.

Figure 9. The variation in mean log-time to rupture with fiber angle for air and benzene environment.

Figure 10. The depth of penetration of benzene with time for pure epoxy resin.

Figure 11. The dependence of depth of penetration of benzene on fiber angle with increasing time.

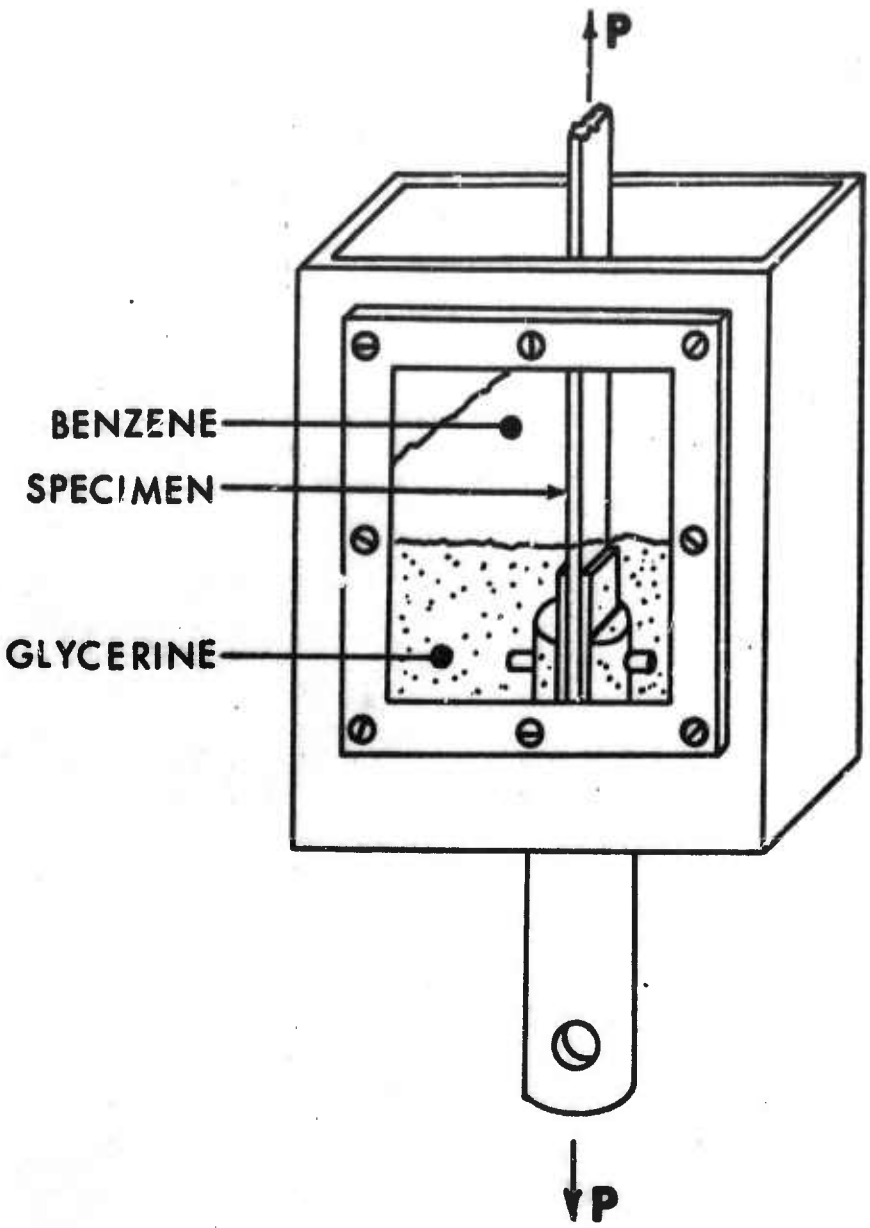


Figure 1. Schematic of environmental testing container and specimen grip assembly.

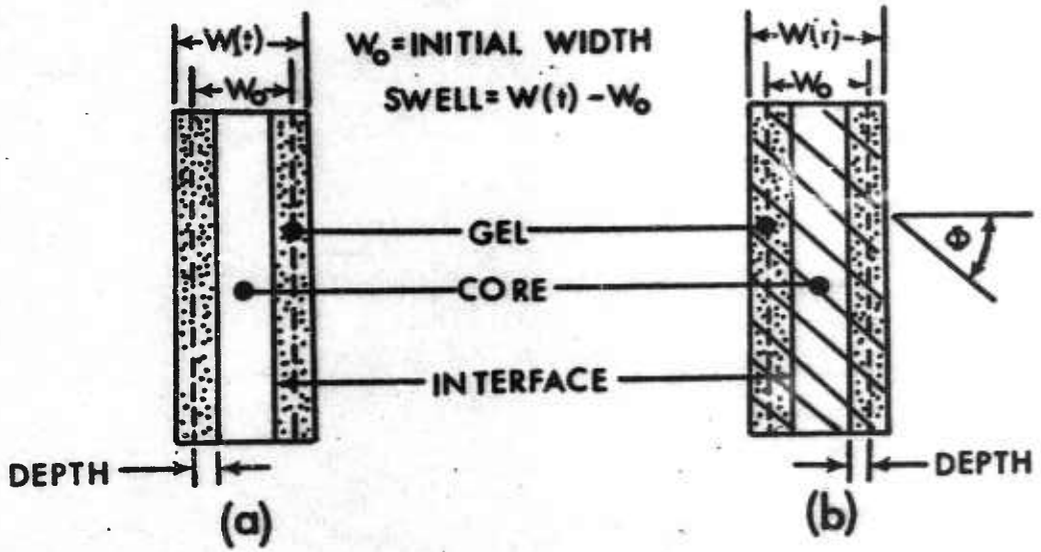


Figure 2. Schematic of specimens during sorption tests showing depth of penetration and swell. (a) Pure epoxy resin (b) Composite specimen.

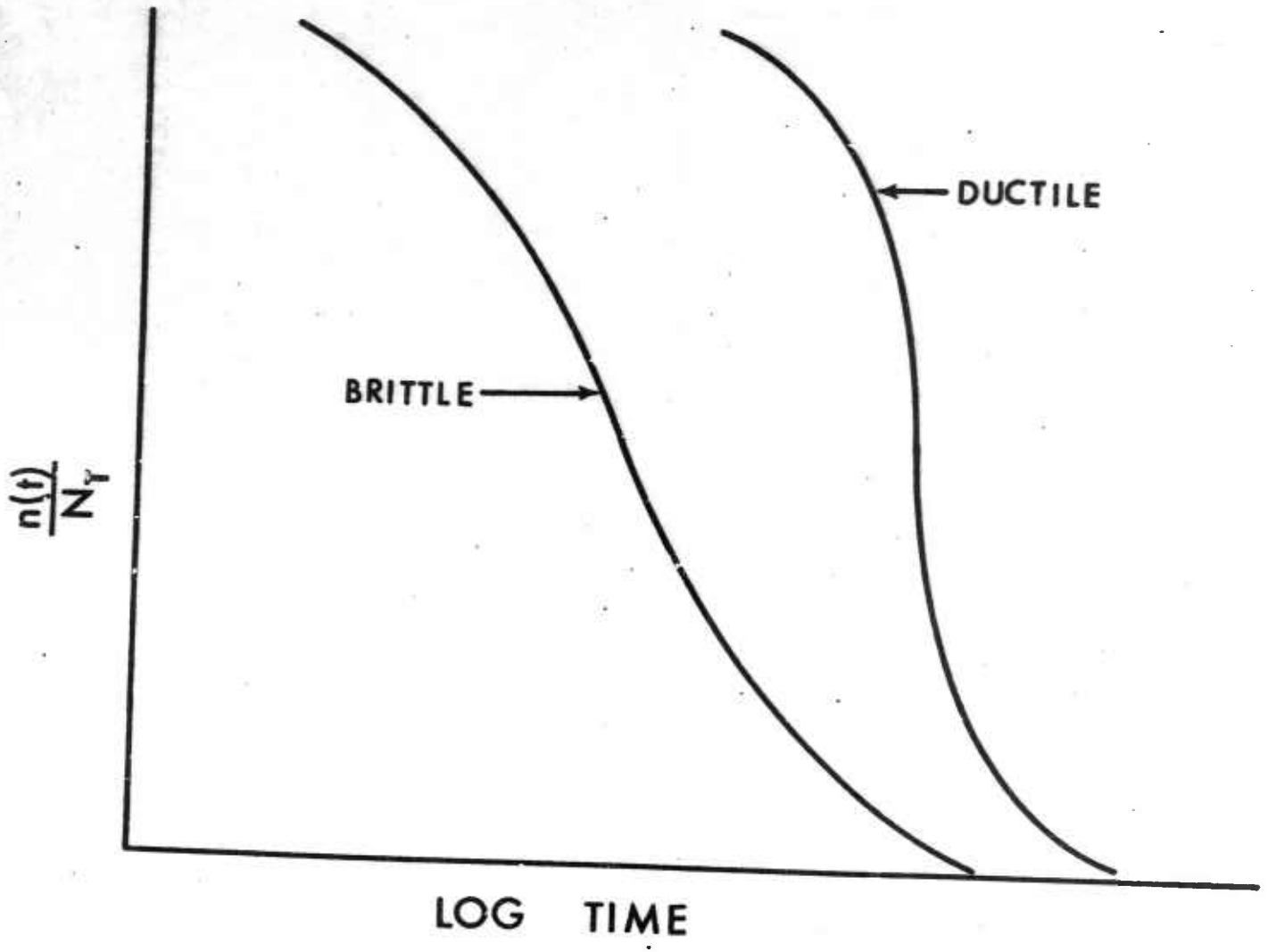


Figure 3. Schematic representation of differences in the cumulative distributions for brittle and ductile rupture (Wu and Halpin [14]).

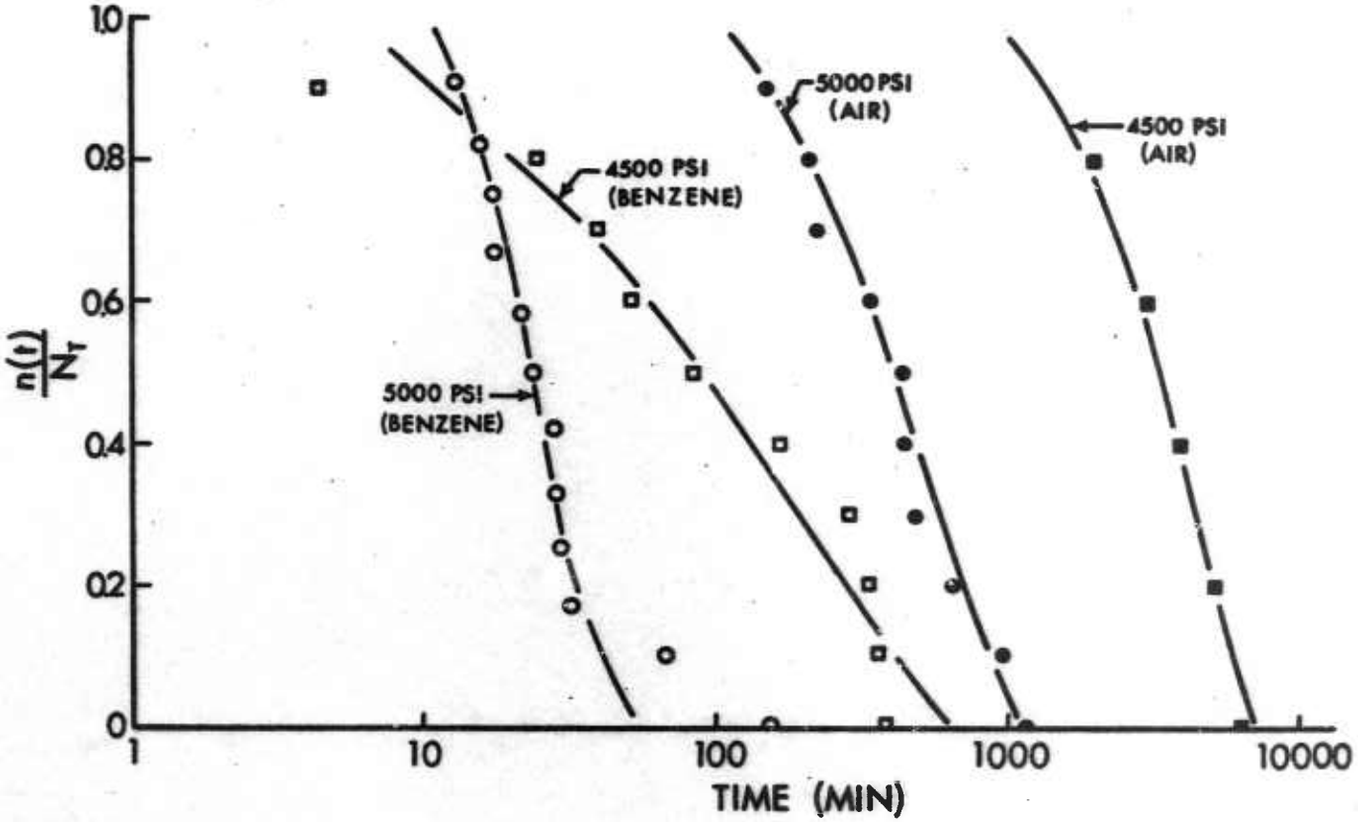


Figure 4. Normalized survival population versus log-time to failure in air and benzene for pure epoxy at stress levels of 4500 and 5000 PSI.

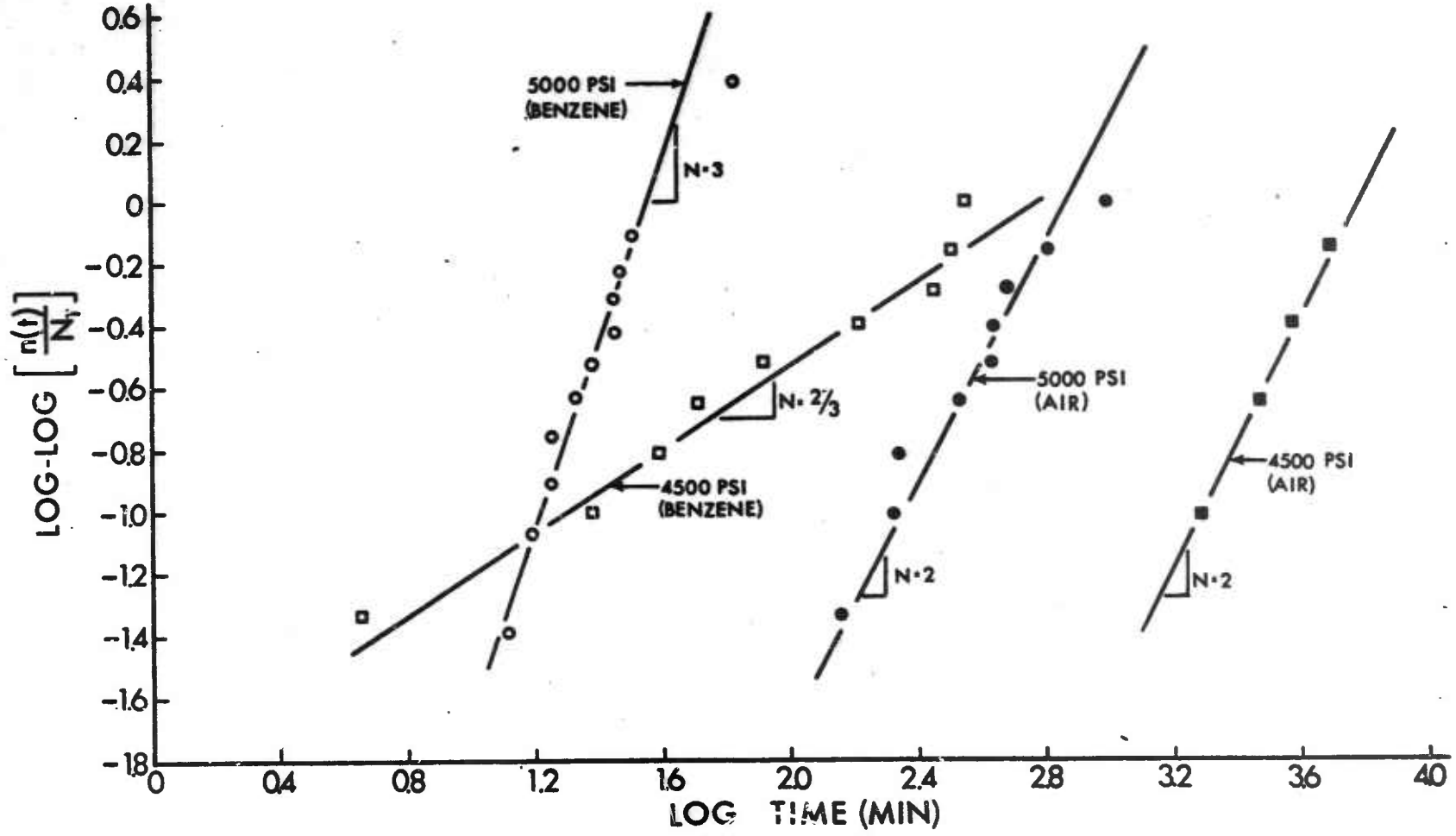


Figure 5. Log-log of the cumulative distribution, $\frac{n(t)}{N_T}$, versus log-time to failure for pure resin at stress levels of 4500 and 5000 PSI in both air and benzene.

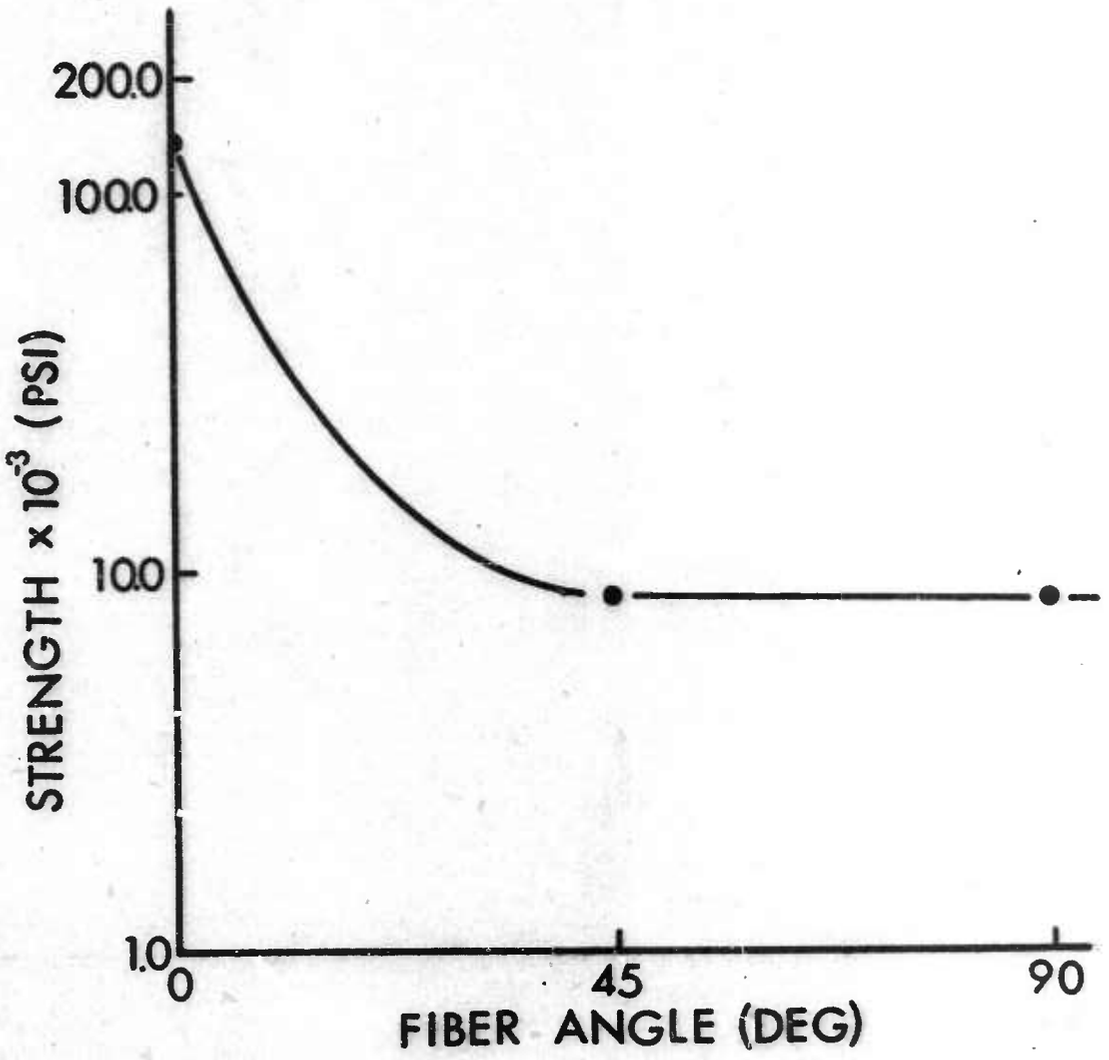


Figure 6. Effect of fiber orientation on the ultimate tensile strength of composite specimens.

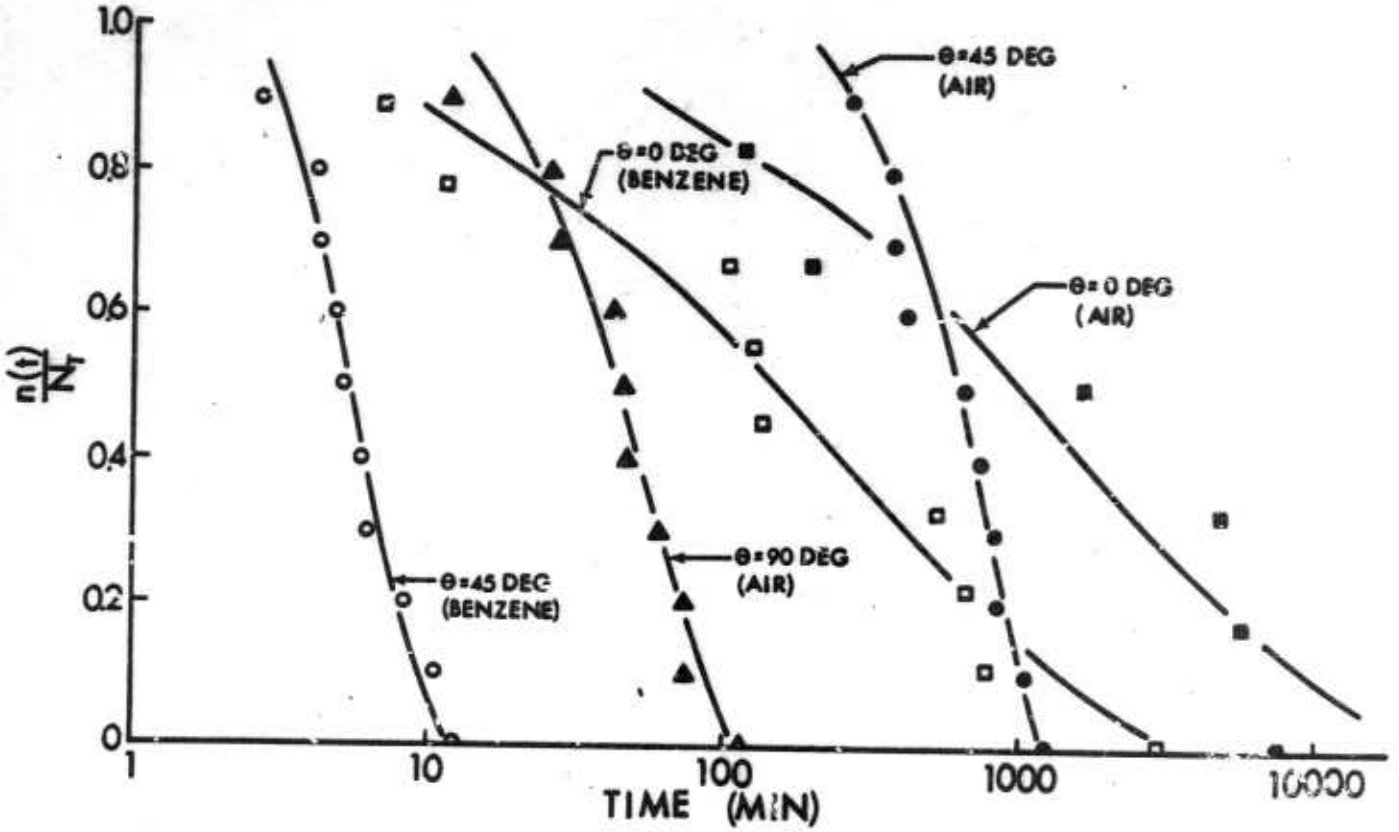


Figure 7. Normalized survival population versus log time to failure in both air and benzene for specimens tested at 79% ultimate tensile strength at each orientation.

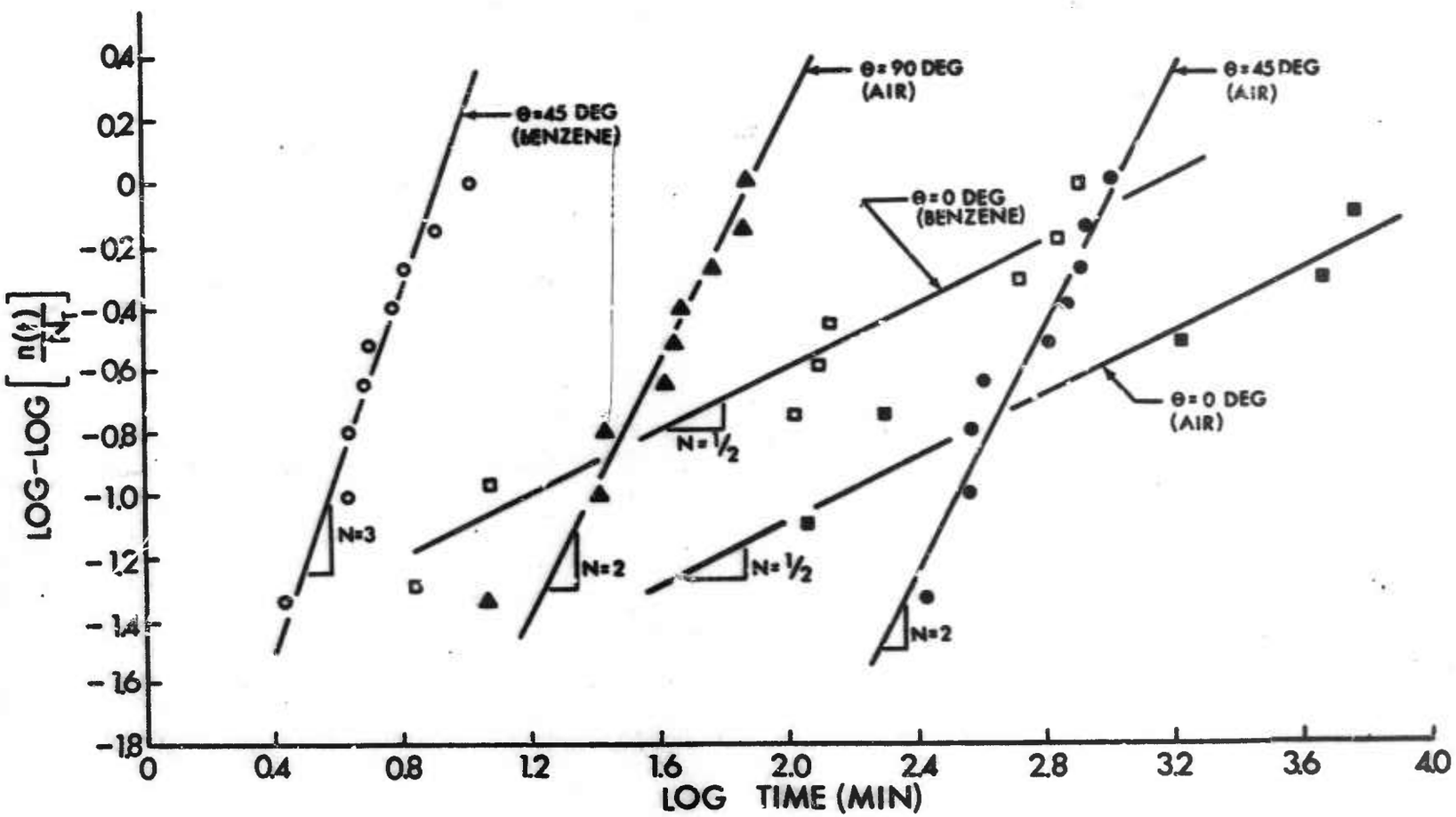


Figure 8. The log log of the cumulative distribution versus log time to rupture for composite specimens texted at 79% ultimate tensile strength for each orientation.

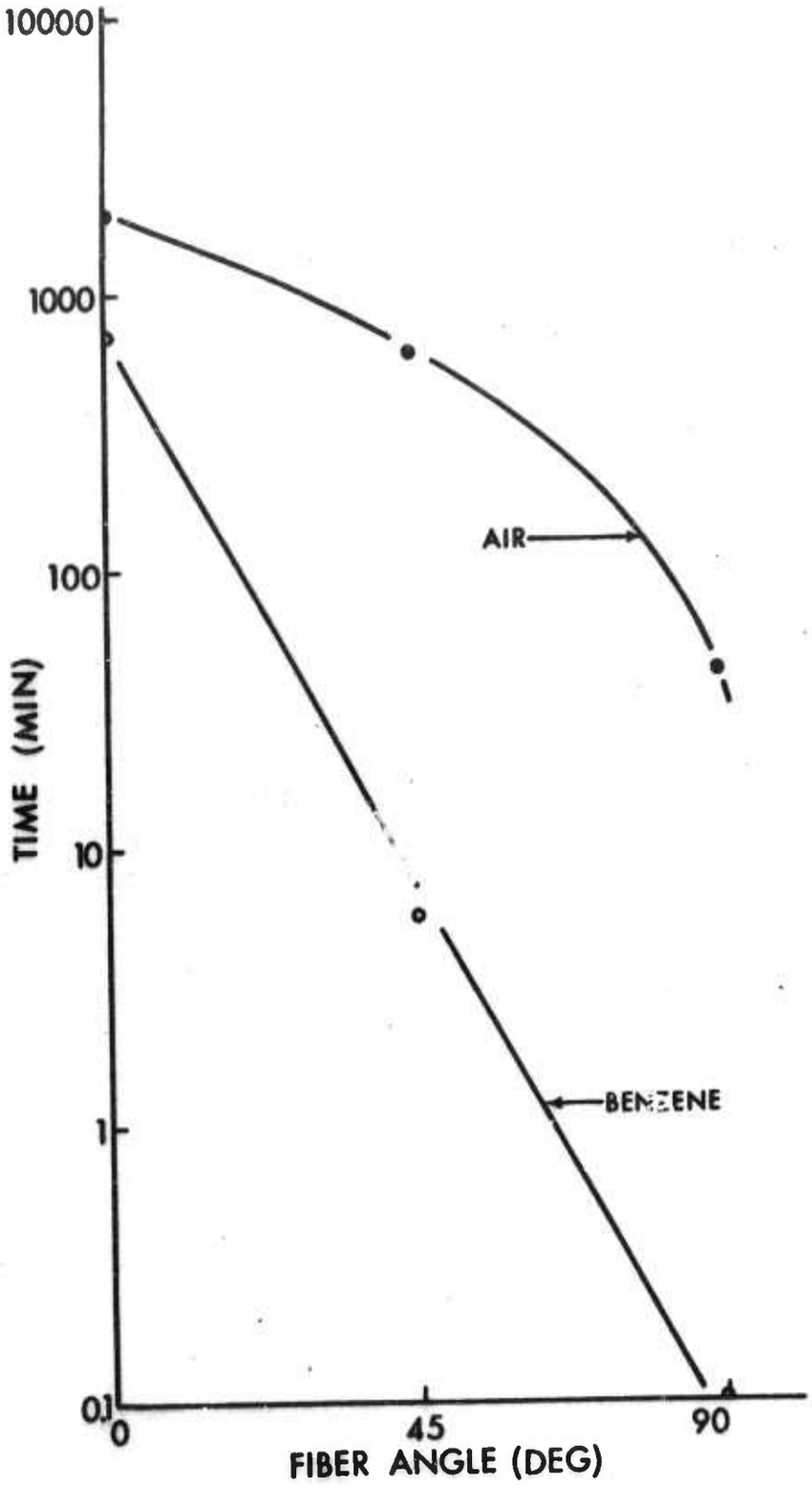


Figure 9. The variation in mean log-time to rupture with fiber angle for air and benzene environment.

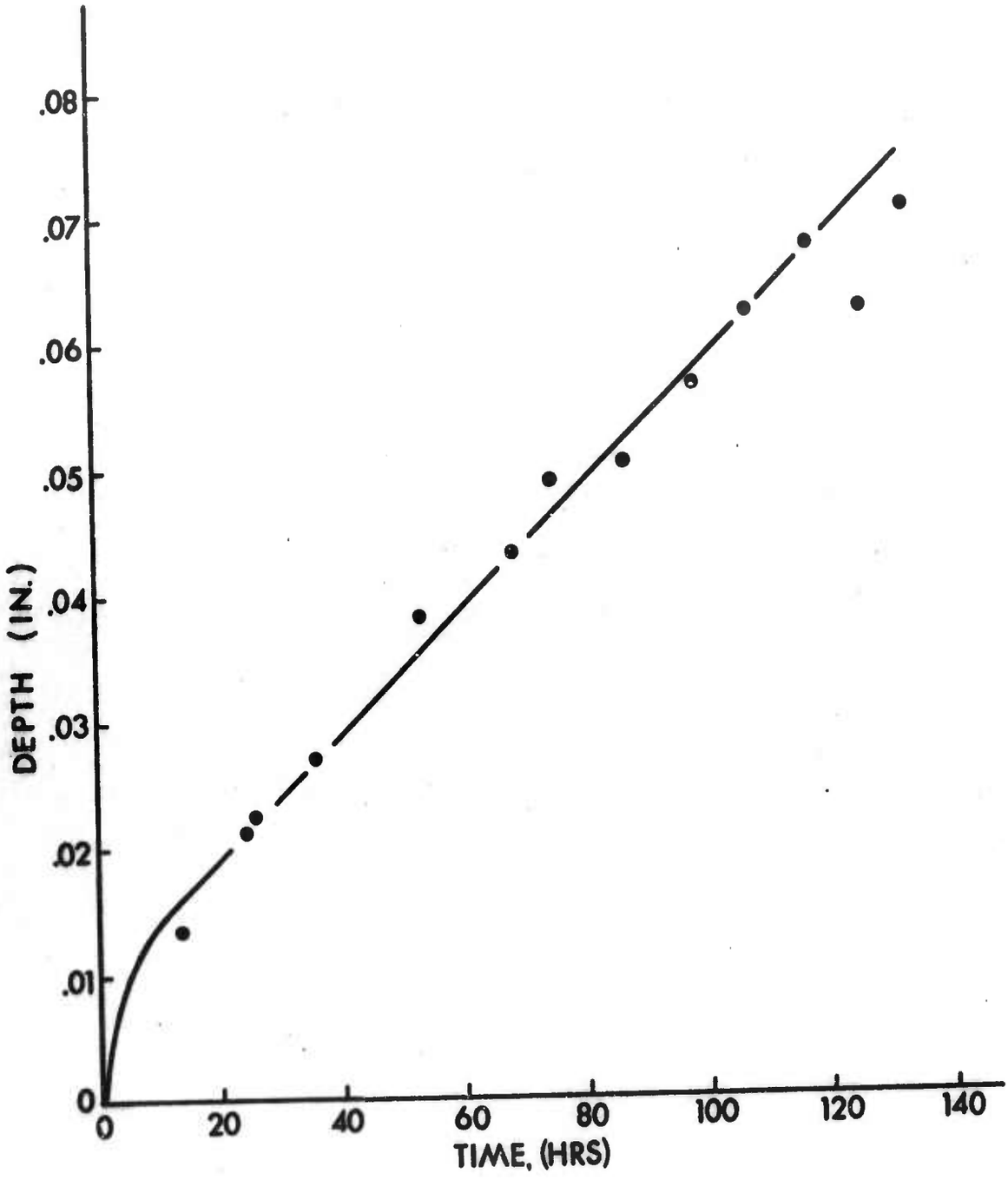


Figure 10. The depth of penetration of benzene with time for pure epoxy resin.

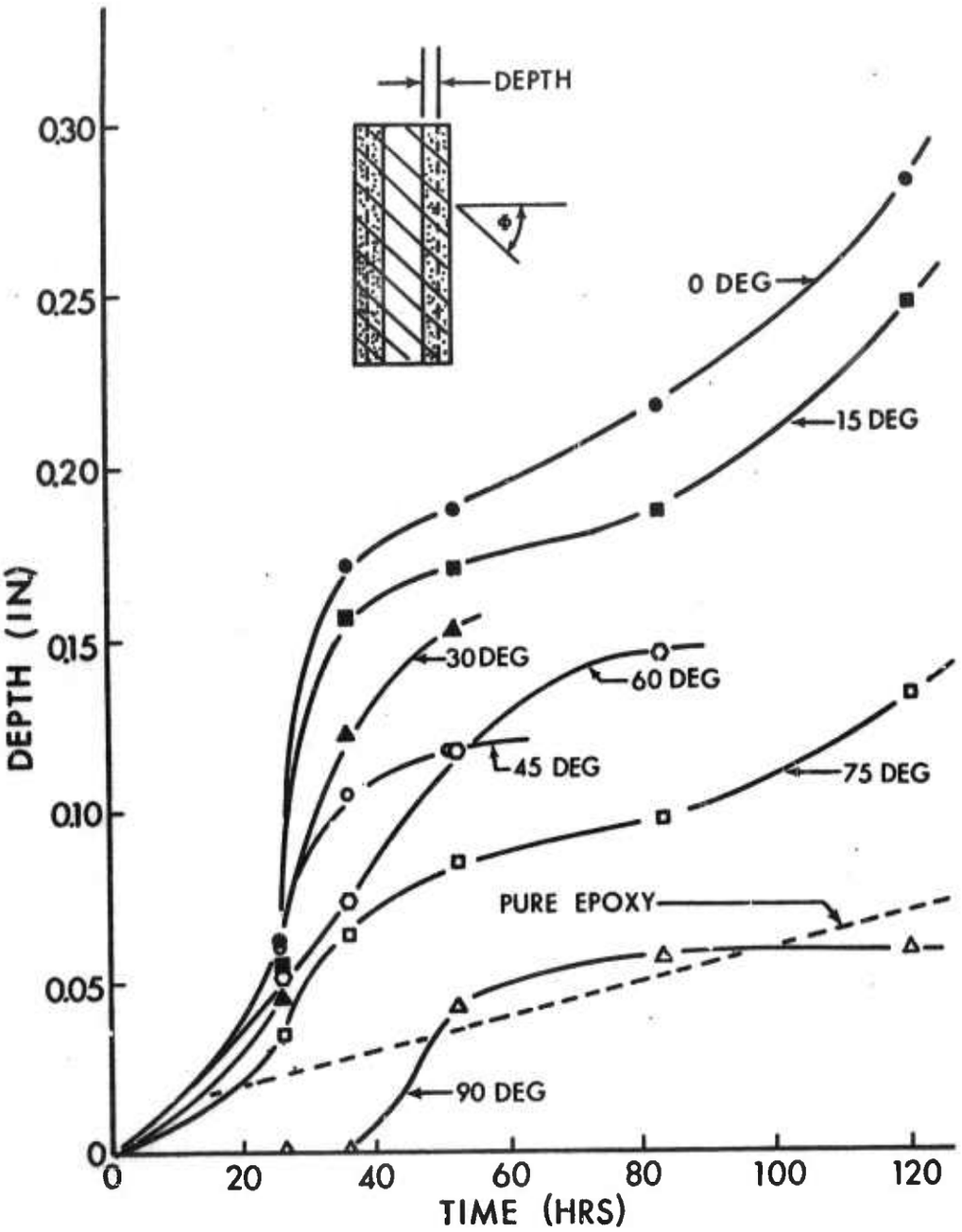


Figure 11. The dependence of depth of penetration of benzene on fiber angle with increasing time.

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13. ABSTRACT

This paper is concerned with the combined effect of an active environment and stress on the survival life of a polymeric composite material. The object of this investigation is to extend the well known kinetic theory of rate-dependent rupture to anisotropic composites in active chemical environments, and to establish the operational technique for one system of environment and composite material. Observations on the statistical variability of the rupture processes are given. The reduction in the life of a homogeneous epoxy matrix (60% Epon 815-40% versamid 140) and that of a unidirectional glass fiber-reinforced epoxy in benzene was experimentally observed for several stress levels. It is hoped that these results can eventually be linked together through micro-mechanics analysis. Significant decreases in survival life of the matrix at several stress levels in the benzene environment were observed. These reductions in life cannot be predicted nor explained from sorption data characterized as Alfrey's Case II transport. Stress rupture experiments were performed for unidirectional composites at 0°, 45° and 90°. Experimental results showed the decrease in life is strongly dependent on the angular orientation of the composite both for the inert and active environment. This suggested a tensorial characteristic must be incorporated into the classical shift factor. Further work required to characterize this anisotropic effect is suggested.

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| unidirectional composites | | | | | | |
| environmental damage | | | | | | |
| organic vapor | | | | | | |
| statistical theory of fracture | | | | | | |
| sorption kinetics | | | | | | |
| swelling stresses | | | | | | |
| shift parameters | | | | | | |